New Approaches to the Preparation of PαMS Beads as Mandrels for NIF-Scale Target Capsules
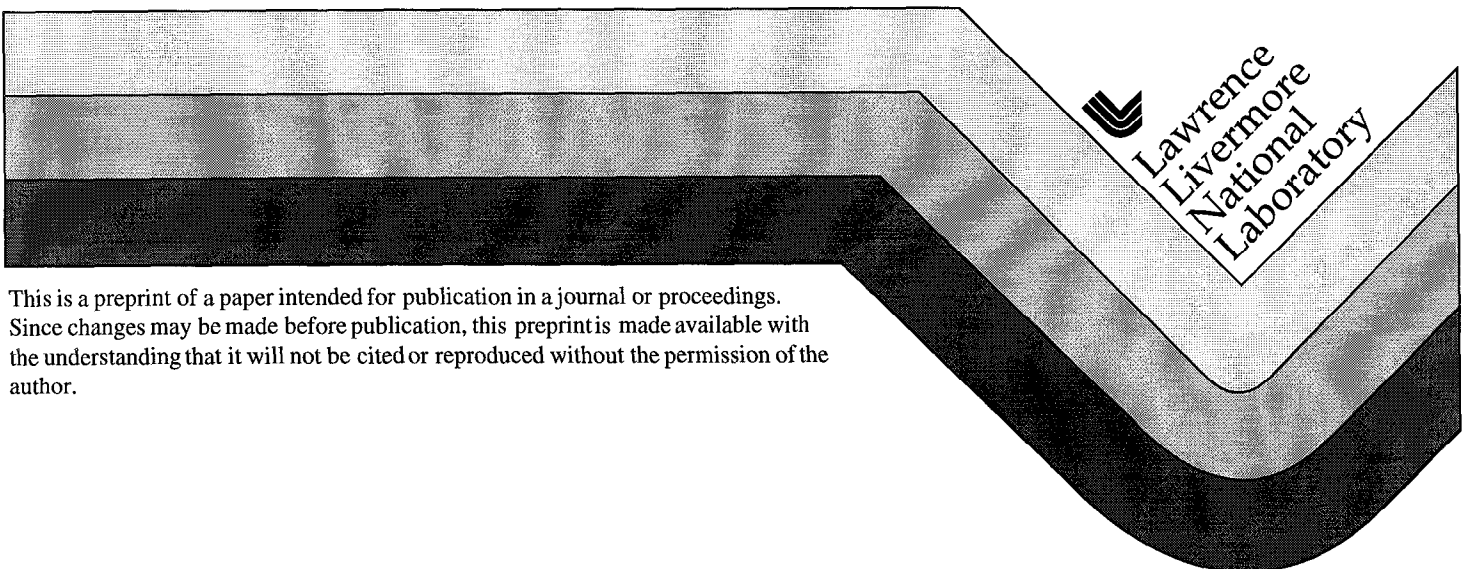
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NEW APPROACHES TO THE PREPARATION OF PαMS BEADS
AS MANDRELS FOR NIF-SCALE TARGET CAPSULES

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ABSTRACT

We report on a new method using heated density gradient columns for preparing spherical poly(α-methylstyrene) (PαMS) bead mandrels for inertial confinement fusion spherical shell targets. Using 1,2 propane diol/glycerol mixtures, stable density gradient columns for supporting PαMS beads can be prepared at temperatures as high as 150 °C. At these temperatures plasticized commercial beads become fluid and spherical, however loss of the plasticizer and very low molecular weight components of the bead due to limited solubility in the column fluid leads to surface finish problems. We also present results on PαMS beads prepared in an aqueous bath batch mode. Using these techniques beads with maximum out-of-rounds less than 5 μm have been produced.

I. INTRODUCTION AND OVERVIEW

The "decomposable mandrel" approach, as currently used for preparing both Nova and Omega scale capsules, involves producing poly(α-methylstyrene) (PαMS) shell mandrels by microencapsulation, overcoating them with plasma polymer, and then thermally processing to decompose the underlying PαMS shell to gas phase monomer which diffuses away leaving a plasma polymer shell with the sphericity of the original PαMS shell. This technique was originally developed using solid PαMS beads,[1] however the ease with which tightly size controlled microencapsulated shells could be prepared with excellent sphericity at Nova and Omega scales, coupled with the advantages due to the decrease in mass to be decomposed, led to the abandoning of the bead work in favor of shells. The extension of the microencapsulation approach to NIF scale shells has proved challenging with respect to maintaining excellent sphericity, and thus we have begun to reexamine the intrinsically simpler bead formation processes as an alternative to PαMS mandrel fabrication.

This paper is divided into two parts. The first describes the use of density gradient columns to process beads in a totally quiescent environment. This approach offers the possibility of eliminating the distorting hydrodynamic forces associated with typical stirred aqueous bath processing.[2] Initial results have been mixed, and will be discussed below. Secondly we have reexamined simple aqueous processing of solid PαMS beads and have been able to prepare 2 mm diameter beads with maximum out-of-round values of less than 10 μm, with a smaller subset having out of round values of less than 5 μm. The results of these experiments will be presented.

II. DENSITY GRADIENT COLUMNS

Our general approach is as follows. A density gradient column whose range includes the density of PαMS at the appropriate processing temperature is prepared from fluids that can be heated to at least 30-50 °C above the glass transition temperature of PαMS. An irregular bead of PαMS of the proper size is placed into the column, the column uniformly heated, allowing the bead to soften and its interfacial surface tension to cause the resulting fluid drop to become spherical after which the column is cooled. The first question to be addressed will be the magnitude of droplet asymmetry that should arise *because of* the density gradient. This will determine how strong a gradient we can tolerate. Following this will be a discussion of how we have tried to experimentally realize the conditions we desire, with a discussion of the initial results and problems encountered.

A. Effect of Density Gradient on Sphericity

Consider a fluid droplet with density ρ_d suspended in a density gradient column as shown in Figure 1. The vertical axis is taken as the z-axis with the zero point as the point where the density of the column fluid matches the density of the droplet. The density gradient in the column is assumed linear and defined by

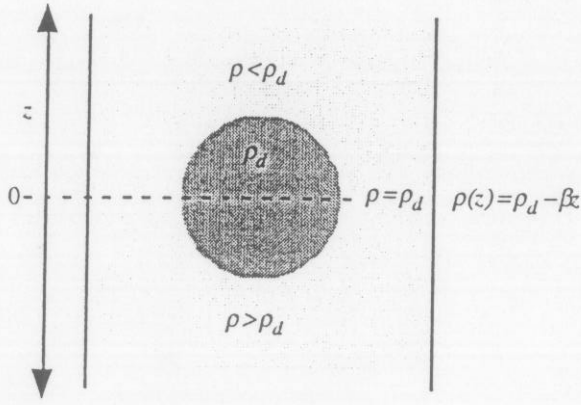$$\rho(z) = \rho_d - \beta z , \qquad (1)$$

Figure 1. Model essentials.

where β is positive and has units of g/cm³cm. This ensures that the density decreases with increasing z.

The next question to address is the nature of the droplet deformation. In the treatment that follows we will assume a symmetric ellipsoidal deformation, which is equivalent to a pure P_2 for small deformations.[3] The deformation must be symmetric due to the linear gradient because of the buoyancy symmetry around $z = 0$ for elements of the fluid drop.

The equation of the symmetric ellipsoid that has the same volume as the reference sphere can be expressed as

$$\frac{x^2 + y^2}{(r+\delta)^2} + \frac{z^2}{\left(\dfrac{r^3}{(r+\delta)^2}\right)^2} = 1 \; , \qquad (2)$$

where r is the radius of the reference perfect sphere and δ is the positive deformation of the droplet radius in the xy plane. It is worth noting that the density gradient column insures a deformation of this sort, the "compression" along the z axis is 4δ (to first order in δ) and thus the maximum out of round, MOOR, is essentially 6δ.

The buoyancy corrected gravitational potential energy of a mass unit, dm, of volume dV, in the droplet can be expressed using eq (1) as

$$d(\text{G.E.}) = dm \times gz = (\rho_d - \rho(z))dV \times gz = \beta g z^2 dV \; , \quad (3)$$

thus the total buoyancy corrected gravitational potential energy of the ellipsoidal droplet is given by

$$\text{G.E.} = \beta g \int_V z^2 dV = \frac{4}{15}\beta g \pi \frac{r^9}{(r+\delta)^4} \; , \qquad (4)$$

where we have used the x,y symmetry to replace the 3-D integration by a 1-D integration of circular slabs of volume $\pi(x^2 + y^2)dz$, and an expression for $(x^2 + y^2)$ in terms of z was determined from eq (2).

The surface energy, S.E., of the ellipsoid is the interfacial surface tension, γ, times the surface area, S_e. The surface area of the oblate ellipsoid described by eq (2) is given by[4]

$$S_e = 2\pi a^2 + \pi \frac{b^2}{\varepsilon} \ln \frac{1+\varepsilon}{1-\varepsilon} \; , \qquad (5)$$

where from eq (2) a and b are the principal radii of the ellipsoid, $a = (r+\delta)$ and $b = r^3/(r+\delta)^2$, and where ε is the eccentricity given by[5]

$$\varepsilon = \frac{\sqrt{a^2 - b^2}}{a} \; . \qquad (6)$$

Because of the complexity of the expression for the surface area in terms of r and δ, it will be useful to rewrite eq (5) as a series expansion in δ to give

$$S_e = 4\pi r^2 + \frac{32\pi}{5}\delta^2 - \frac{352\pi}{105r}\delta^3 + O\left(\delta^4\right) \; . \qquad (7)$$

Thus the total energy is the sum of the gravitational and surface energy contributions, and this can be minimized with respect to δ to determine the droplet deformation, the result being

$$\delta = \frac{g\beta r^4}{5g\beta r^3 + 12\gamma} \cong \frac{g\beta r^4}{12\gamma} \; , \qquad (8)$$

thus the MOOR is

$$\text{MOOR} = \frac{g\beta r^4}{2\gamma} \; . \qquad (9)$$

This expression allows us to evaluate what values of β, which characterizes the density gradient, are acceptable. If we want the shell to be less than 1 μm out of round then δ must be less than 1/6 μm or 0.16×10^{-4} cm. Using 0.1 cm for r and 10 dyne/cm for γ, we find that β must be no greater than about 0.02 g/cm³cm. Thus on a 10 cm high column the density at the top must be no greater than 0.2

g/cm³ more than the density on the bottom. This is easy to accomplish.

B. Experimental Results

In the preliminary experiments described here, we constructed a "column" in a small test tube by layering approximately 1 cm thick layers of six solutions of 1,2-propylene glycol/glycerol with compositions as shown in Table I. There is a range of materials that we considered, the primary limiting factors are that they must be immiscible with PαMS and have a relatively high boiling point. The solution densities were calculated from the volume fractions of the components assuming ideal solutions, and the densities given are at 20 °C. This range was selected because it was sure to bracket the PαMS density at any relevant temperature. Clearly when heated the density of each layer (and the PαMS bead/droplet) will decrease.

Table I. Volume fractions of 1,2-propylene glycol (PPG, ρ = 1.0361 g/cm³) and glycerol (GLY, ρ = 1.2613 g/cm³) and the computed densities of the initial layers in the column.

Volume Fractions		mix ρ
PPG	GLY	(g/cm³)
1.00	0.00	1.0361
0.90	0.10	1.0586
0.80	0.20	1.0811
0.70	0.30	1.1037
0.60	0.40	1.1262
0.50	0.50	1.1487

After the solutions were layered in the test tube it was submerged into mineral oil held at about 150 °C and allowed to come to thermal equilibrium. It is expected that under these conditions the abrupt density changes at the layer interfaces "smooth", in the ideal limit a nearly linear density gradient might be obtained. In these initial experiments no detailed analysis of the time dependent gradient was made, however, it was determined that the gradient was sufficiently stable at 150 °C to support a PαMS droplet for at least 24 h. A solid PαMS bead of appropriate size is inserted into the column, it falls to a neutrally buoyant position where it softens and becomes spherical. After 4 h the column is cooled and the hardened bead recovered and characterized.

The beads used for this study were commercially available PαMS (Scientific Polymer Products) with a stated molecular weight (MW) of 11K Daltons. The beads are composed of a broad MW distribution, including a large fraction of very low MW material (< 500 Daltons) that

serves to plasticize the polymer, lowering its glass transition temperature to about 50-60 °C from the literature value for PαMS of about 170 °C.[6] The details of the bead composition will be described shortly. At this point we only wish to point out that this plasticization is necessary for the current experiments in order to allow the beads to become fluid at the column temperature of 150 °C.

A set of beads was treated in the above-described column at 150 °C for 4 h. If one assumes that the gradient was in fact linear (best possible case) its value, β, would be about 0.0225 g/cm³cm, and using an interfacial surface tension, γ, of 10 dynes/cm (a guess) one can calculate that a 2 mm diameter bead would be about 1 µm out of round. Clearly the gradient should be reduced, and this is feasible, but in addition we need to initially produce a linear gradient (rather than steps) using well-defined procedures. The point here is that the best we could hope for are beads about 1 µm out of round, and probably significantly more since the gradient the bead actually felt was more than the above calculation due to the initial step construction. Table II presents data for 8 single bead experiments. The measurements were made by digitally capturing the shadow of a bead and determining its perimeter. Accuracy is probably not better than 1-2 µm, but is adequate as a screening tool for these preliminary experiments. Three roughly orthogonal shadowgrams for bead BC8 are shown in Figure 2. The large single point excursions are due in large part to significant surface debris. As described below, determining the cause of this debris has been a main concern, and because of this optimization of bead sphericity has not yet been accomplished.

We have determined that the debris problem is due to the fact that the highly plasticized, low molecular weight 11K PαMS bead material we are using has some solubility in the hot column fluids. This was signaled initially by the formation of a white "fog" around the bead

Table II. Beads treated for 4 h in 6-step column at 150 °C. Bead diameters from 1.8 to 1.9 mm. Measurements for beads BC9-16 are based on a single orientation shadowgram.

Bead ID	MOOR (µm)
BC8	6.3
BC9	14.5
BC10	6.3
BC12	4.1
BC13	16.2
BC14	10.5
BC15	14.0
BC16	10.6

when the column cooled, a significant amount of the material redepositing upon the bead resulting in a rough, debris laden surface. To explore the situation further, we made careful mass measurements of the beads before and after exposure to the 150 °C column for various periods of time. The results are displayed in Figure 3. Three trials were completed for each time.
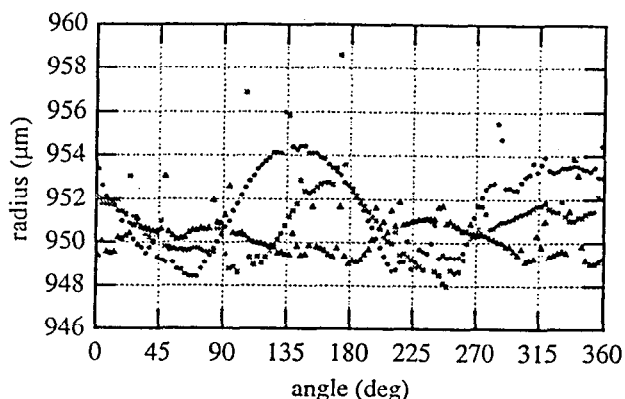

Figure 2. Three orthogonal shadowgram traces from bead BC8. The apparent "noise" is due to surface debris.
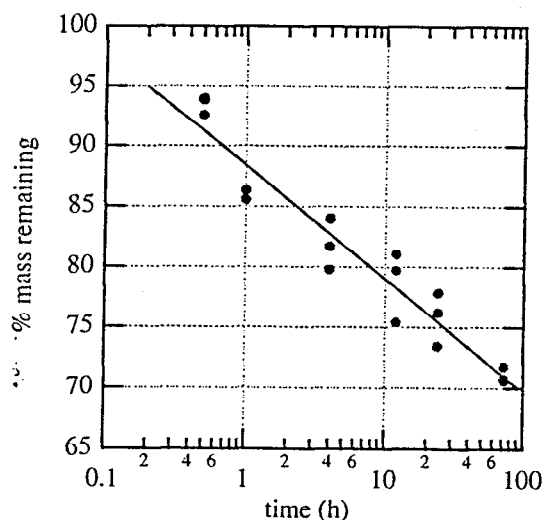

Figure 3. Mass loss in column as a function of time.

The data in Figure 3 shows significant mass loss during heating. We determined *what* was being lost by using Gel Permeation Chromatography (GPC) to examine the material before and after column heating. In Figure 4 the GPC data for the untreated 11K PαMS bead is displayed, along with spikes for polystyrene MW standards ranging from 1.3K to 165K. The untreated 11K PαMS material is composed of a broad distribution of polymeric material with MW's up to 60K, and a significant amount of material (presumably the plasticizer) with MW less than

1K. The resolved peaks on the right side may be due to individual PαMS oligomers, but this has not been confirmed. Also shown in Figure 4 are the GPC data for beads BC26 and BC27, which were treated 1.0 and 24.0 h, respectively, in the 150 °C column. In addition, data for a sample of polymer that was reprecipitated once to remove low molecular weight components is also shown. Clearly heat treatment is removing the very low molecular weight material by providing limited solubility at elevated temperatures. When the column is cooled the solubility limit of this material is apparently exceeded and it redeposits on the bead.
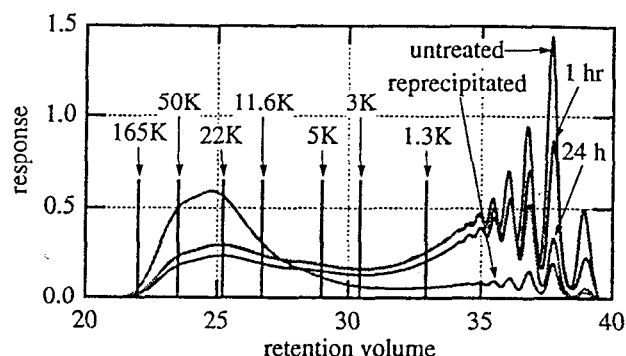

Figure 4. GPC measurements on 4 PαMS samples. The vertical spikes show the molecular weight calibration (polystyrene standards). Shown is the data for the untreated and reprecipitated PαMS. The other two samples were column heat treated for 1 and 24 h, respectively.

At this point we have not solved the dissolution and debris problem. One approach would be to use PαMS beads that don't have the low molecular weight component. However, as noted above, the glass transition temperature of unplasticized moderate to high molecular weight PαMS is about 170 °C and thus would require a column temperature of at least 220 °C, higher would be better. Glycerol decomposes at 290 °C and is thus feasible, however 1,2-propylene glycol boils at 189 °C and is thus not suitable for a higher temperature column. One option we plan to explore is the use of 2-ethyl-1,3-hexanediol, which has a density of 0.9325 g/cm^3 at 25 °C and a boiling point of 244 °C. A column constructed of glycerol and 2-ethyl-1,3-hexanediol may be able to handle temperatures up to 230 or 240 °C, making the use of unplasticized PαMS possible.

III. AQUEOUS BATH BATCH PROCESSING

The early work of Letts, et al.[1] on the decomposable mandrel approach to plastic shells used simple hot water batch processing of the highly plasticized, low MW PαMS

beads. Careful sphericity characterization was limited in general to sub mm size beads; thus our purpose in revisiting this approach was to determine what could be achieved for 2-mm beads. The original work was done with both 11K and 19K commercial PαMS beads (Scientific Polymer Products), which have glass transition temperatures of about 60 and 90 °C respectively, as measured by Thermal Mechanical Analysis (TMA) at LLNL. In the work reported here we have used the 19K beads.

The approach is similar to what has previously been done. A batch (10's) of beads with diameters between 0.5 and 3 mm are placed in a 1% aqueous solution of PVA and heated to 96 °C for 8.5 h while the bath solution is stirred at 160 rpm with a three blade scoping propeller 0.5 inch from the bottom of the beaker. The bath is allowed to cool while still being stirred, after which the beads are rinsed and air-dried. A selection of 10 beads approximately 2 mm in diameter were then characterized by shadowgraphy; the results are displayed in Table III. Each bead was measured in three orthogonal orientations, and the results shown for each bead represent the maximum diameter difference of the three measurements. As noted above, the net accuracy of the MOOR is probably no better than a couple of microns, but does give a quick and good basis for more careful characterization. Clearly some of these beads are only a few μms out of round, perhaps close to NIF quality.

The 1901 μm diameter bead was characterized on our AFM-based Spheremapper.[7] In this technique the capsule, supported on a vacuum chuck, is rotated while an AFM records the circumferential surface profile. Typically three traces, 40 μm apart, are taken at each of three orthogonal capsule orientations. The average of the square of the amplitudes of the k mode components of the Fourier transforms of these traces describes the surface finish of the capsule in terms of its 1-D power spectrum.[7] One set of traces for the 1901 μm diameter bead is shown in Figure 5. In each pair of traces the upper trace is the original AFM trace. Because the large debris spikes give rise to significant power at all modes, in the lower traces we have mathematically removed the large debris in order to get a better look at the intrinsic sphericity of the bead. The power spectra for the "dirty" and "cleaned" beads are shown in Figure 6, along with the power spectrum goal for NIF capsules.[8] Clearly additional improvement is needed. There is still significant roughness at all modes; the more serious low to middle mode roughness is clearly visible in the wiggles in the trace data. Work is planned to optimize the technique with respect to heating time, bath temperature, and agitation technique to see if the level of sphericity we need can be obtained.

Table III. Beads treated for 8.5 h in batch mode in 96 °C water. Shown are the bead diameter and the maximum out of round from three orthogonal orientation shadowgrams.

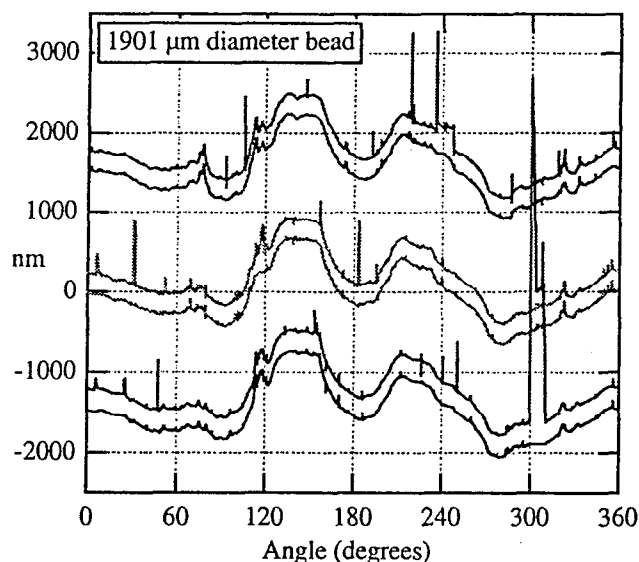| Diameter (μm)	MOOR (μm)
1858	3
1862	1
1901	2
1902	4
1929	3
2049	4
2068	5
2080	2
2084	9
2170	3

Figure 5. One set of AFM traces from the 1901 μm diameter aqueous bath processed bead. The upper trace in each pair is the original data; the lower trace has been mathematically "cleaned" to remove much of the high frequency debris.
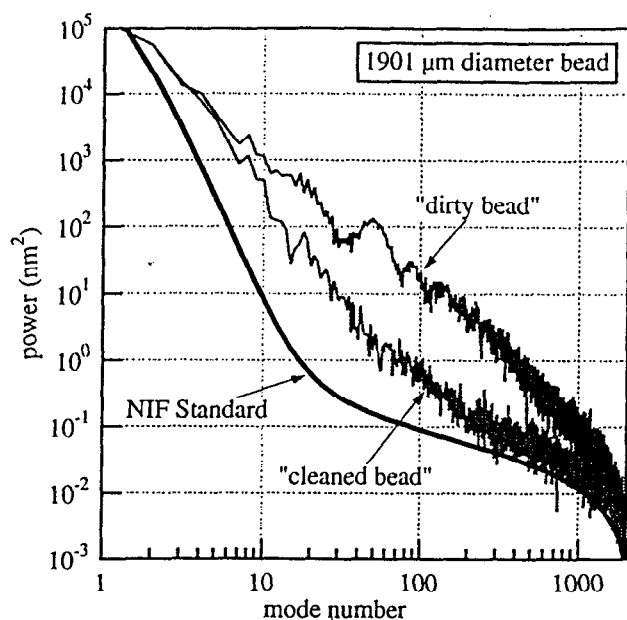
Figure 6. Power spectra generated from the complete set of 9 traces from the 1901 μm diameter bead, both before (dirty) and after (cleaned) mathematical debris removal as shown in Figure 5. Also shown is the NIF goal.

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